

Nickel-based superalloy having high resistance to hot-corrosion for monocrystalline blades of industrial turbines

TECHNICAL FIELD

The invention relates to a nickel-based superalloy which is adapted to the manufacture of fixed and movable monocrystalline blades of industrial gas turbines by directional solidification.

BACKGROUND OF THE INVENTION

Nickel-based superalloys are the most high-performance materials used today in the manufacture of movable and fixed blades of industrial gas turbines. The two principal features required until now of these alloys for those specific applications have been good resistance to creep at temperatures of up to 850°C and very good resistance to hot-corrosion. Some reference alloys currently used in this field are designated IN738, IN939 and IN792.

Blades manufactured using those reference alloys are produced by conventional casting using the lost-wax process and have a polycrystalline structure, that is to say, they are constituted by the juxtaposition of crystals which are orientated in a random manner relative to each other and which are called grains. Those grains are themselves constituted by an austenitic matrix gamma ( $\gamma$ ) based on nickel, in which hardening particles of the phase gamma prime ( $\gamma'$ ) are dispersed whose base is the intermetallic compound  $\text{Ni}_3\text{Al}$ . This specific structure of the grains gives those alloys a high level of creep resistance up to temperatures in the order of 850°C, which ensures the longevity of the blades, for which service lives of from 50,000 to 100,000 hours are generally

sought. The chemical composition of alloys IN939, IN738 and IN792 has further been determined to give them excellent resistance to the combustion gas environment, in particular in respect of hot-corrosion, a phenomenon which is particularly aggressive in the case of industrial gas turbines. Significant additions of chrome, typically of from 12 to 22% by weight, are thus necessary to give those alloys the necessary resistance to hot-corrosion for the applications concerned. From the point of view of resistance to creep, the order of the alloys is:  $IN939 < IN738 < IN792$ . From the point of view of resistance to hot-corrosion, the order is the reverse, that is:  $IN792 < IN738 < IN939$ .

In order to improve the performance of industrial gas turbines in terms of output and consumption, one method consists in increasing the temperature of the gases at the turbine inlet. This consequently makes it necessary to be able to provide alloys for turbine blades which can tolerate operating temperatures which are higher and higher, whilst retaining the same mechanical features, in particular in terms of creep, in order to be able to achieve the same service lives.

The same type of problem has been posed in the past in the case of gas turbines for turbo-jets and turbo-engines for aeronautical applications. In this case, the selected solution consisted in changing from blades, known as polycrystalline blades, which are produced by conventional casting to blades, known as monocrystalline blades, that is to say, which are constituted by a single metallurgical grain.

Those monocrystalline blades are manufactured by directional solidification with lost-wax casting. The elimination of grain boundaries, which are preferential locations for creep

deformation at elevated temperature, has allowed the performance of nickel-based superalloys to be increased spectacularly. Furthermore, the process of monocrystalline solidification allows the preferred orientation of growth of the monocrystalline component to be selected and, in that manner, the orientation  $\langle 001 \rangle$  which is optimum from the point of view of resistance to creep and thermal fatigue to be chosen, those two types of mechanical stress being the most disadvantageous for turbine blades.

However, the chemical superalloy compounds developed for monocrystalline turbine blades for aeronautical applications are not suitable for blades for terrestrial or marine applications, known as industrial applications. Those alloys are determined in order to promote their mechanical resistance up to temperatures greater than  $1100^{\circ}\text{C}$ , and this to the detriment of their resistance to hot-corrosion. In that manner, the concentration of chrome of the superalloys for aeronautical monocrystalline turbine blades is generally less than 8% by weight, which allows volume fractions of the  $\gamma'$  phase in the order of 70% to be achieved, which levels are advantageous for resistance to creep at elevated temperature.

A nickel-based superalloy which is rich in chrome and which is suitable for the monocrystalline solidification of components of industrial gas turbines is known by the designation SC16 and is described in FR 2 643 085 A. Its concentration of chrome is equivalent to 16% by weight. The features concerning the creep resistance of alloy SC16 are such that the alloy provides, relative to the polycrystalline reference alloy IN738, an increase in operating temperature ranging from approximately  $30^{\circ}\text{C}$  ( $830^{\circ}\text{C}$  instead of  $800^{\circ}\text{C}$ ) to approximately  $50^{\circ}\text{C}$  ( $950^{\circ}\text{C}$  instead of  $900^{\circ}\text{C}$ ). Comparative tests for cyclical corrosion at  $850^{\circ}\text{C}$  in air at atmospheric pressure

with  $\text{Na}_2\text{SO}_4$  contamination showed that the resistance to hot-corrosion of alloy SC16 was at least equivalent to that of the reference polycrystalline alloy IN738.

Hot-corrosion tests have been carried out on alloy SC16 by the manufacturers of industrial turbines on their own test benches. In very severe environments, which are representative of extreme operating conditions, it has been shown that the resistance to hot-corrosion of that alloy remained inferior to that of alloy IN738.

Furthermore, the increasing demand from those manufacturers for an increase in the operating temperature of gas turbines gives rise to the need for superalloys for blades to have a resistance to creep which is increased still further.

#### SUMMARY OF THE INVENTION

The problem addressed by the invention is to provide a nickel-based superalloy having a resistance to hot-corrosion in the aggressive combustion gas environment of industrial gas turbines which is at least equivalent to that of reference polycrystalline superalloy IN792, and having a resistance to creep which is greater than or equal to that of reference alloy IN792 within a temperature range of up to  $1000^\circ\text{C}$ .

This superalloy must in particular be suitable for manufacture of fixed and movable monocrystalline blades having large dimensions (up to several tens of centimetres in height) of industrial gas turbines by directional solidification.

Furthermore, this superalloy must demonstrate good microstructural stability in respect of the precipitation of fragile intermetallic phases which are rich in chrome when maintained for sustained periods at elevated temperature.

More specifically, an alloy compound is sought which ensures:

- optimised resistance to hot-corrosion, in any case at least equivalent to that of reference polycrystalline superalloy IN792, and this in various environments which are representative of that for combustion gases of industrial turbines;
- a maximum volume fraction of hardening precipitates of the  $\gamma'$  phase in order to promote resistance to creep at elevated temperature;
- resistance to creep up to  $1000^{\circ}\text{C}$  which is superior to that of reference polycrystalline alloy IN792;
- a tendency to homogeneity by completely placing in solution particles of the  $\gamma'$  phase, including the  $\gamma/\gamma'$  eutectic phases;
- the absence of precipitation of fragile intermetallic phases which are rich in chrome, starting from the  $\alpha$  matrix, when maintained for sustained periods at elevated temperature;
- a density which is less than  $8.4 \text{ g.cm}^{-3}$  in order to minimise the mass of the monocrystalline blades and, consequently, to limit the centrifugal stress acting on the blades and on the turbine disc to which they are fixed;
- a good tendency to monocrystalline solidification of turbine blades whose height can reach several tens of centimetres and the mass several kilograms.

The superalloy according to the invention, which is suitable for monocrystalline solidification, has the following composition by weight:

Co:	4.75	to	5.25%
Cr:	11.5	to	12.5%
Mo:	0.8	to	1.2%
W:	3.75	to	4.25%
Al:	3.75	to	4.25%
Ti:	4	to	4.8
Ta:	1.75	to	2.25%
C:	0.006	to	0.04%
B:		≤	0.01%
Zr:		≤	0.01%
Hf:		≤	1 %
Nb:		≤	1 %

Ni and any impurities: complement to 100%.

The alloy according to the invention is an excellent compromise between resistance to creep and resistance to hot-corrosion. It is suitable for the manufacture of monocrystalline components, that is to say, components which comprise a single metallurgical grain. This specific structure is obtained, for example, by means of a conventional directional solidification process at a thermal gradient, using a helical or chicane-like device for selecting a grain, or a monocrystal nucleus.

The invention also relates to an industrial turbine blade which is produced by monocrystalline solidification of the above superalloy.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The features and advantages of the invention will be set forth in greater detail in the description below with reference to the appended drawings.

Figures 1 and 2 are graphs illustrating the properties of different superalloys.

#### DETAILED DESCRIPTION

An alloy according to the invention designated SCB444 has been produced with reference to the nominal composition listed in Table I. In this Table, the nominal concentrations of major elements of reference alloys IN939, IN738, IN792 and SC16 are also listed.

Table I: Concentrations by weight of major elements (%)

Alloy	Ni	Co	Cr	Mo	W	Al	Ti	Ta	Nb
IN939	Base	19	22.5	-	2	1.9	3.7	1.4	1
IN738	Base	8.5	16	1.7	2.6	3.4	3.4	1.7	0.9
IN792	Base	9	12.4	1.9	3.8	3.1	4.5	3.9	-
SC16	Base	-	16	3	-	3.5	3.5	3.5	-
SCB444	Base	5	12	1	4	4	4.4	2	-

Chrome has an advantageous and dominant effect on the resistance to hot-corrosion of nickel-based superalloys. Thus, tests have shown that a concentration in the order of 12% by weight was necessary and sufficient in the alloy of the invention in order to obtain resistance to hot-corrosion that is equivalent to that of reference alloy IN792 under the conditions for hot-corrosion tests described below, which conditions are representative of the environment created by combustion gases of some industrial turbines. A higher chrome content would not allow the volume fraction of the  $\gamma'$  phase, which is necessary for good creep resistance of the alloy up to 1000°C, to be reached without the alloy becoming

unstable in respect of the precipitation of fragile inter-metallic phases which are rich in chrome in the  $\gamma$  matrix. Chrome also contributes to the hardening of the  $\gamma$  matrix in which this element is preferentially distributed.

Molybdenum greatly hardens the  $\gamma$  matrix in which the element is preferentially distributed. The quantity of molybdenum which can be introduced to the alloy is limited, however, because the element has a disadvantageous effect on the resistance to hot-corrosion of nickel-based superalloys. A concentration in the order of 1% by weight in the alloy of the invention is not detrimental to the corrosion resistance and contributes significantly to its hardening.

Cobalt also contributes to the hardening in the form of a solid solution of the  $\gamma$  matrix. The concentration of cobalt has an effect on the dissolution temperature of the  $\gamma'$  hardening phase ( $\gamma'$  solvus temperature). Thus, it is advantageous to increase the concentration of cobalt in order to decrease the solvus temperature of the  $\gamma'$  phase and to facilitate the homogenising of the alloy by means of heat treatment without any risk of causing melting to start. Furthermore, it can also be advantageous to reduce the concentration of cobalt in order to increase the solvus temperature of the  $\gamma'$  phase and to benefit in that manner from greater stability of the  $\gamma'$  phase at elevated temperature, which promotes resistance to creep. A concentration in the order of 5% by weight of cobalt in the alloy of the invention leads to an optimum compromise between a good capacity for homogenising and good resistance to creep.

Tungsten, whose concentration is in the order of 4% by weight in the alloy of the invention, is distributed in a



substantially equal manner between the  $\gamma$  and  $\gamma'$  phases and, in that manner, contributes to the respective hardening processes thereof. Its concentration in the alloy is, however, limited because the element is heavy and has a negative effect on the resistance to hot-corrosion. -

The concentration of aluminium is in the order of 4% by weight in the alloy of the invention. The presence of the element causes the precipitation of the  $\gamma'$  hardening phase. Aluminium also promotes resistance to oxidation. The elements titanium and tantalum are added to the alloy of the invention in order to reinforce the  $\gamma'$  phase in which they are substituted for the element aluminium. The respective concentrations of those two elements in the alloy of the invention are in the order of 4.4% by weight for titanium and 2% by weight for tantalum. Under the conditions for hot-corrosion tests described below, corresponding to the intended application, tests showed that the presence of titanium was more favourable to the resistance to hot-corrosion than was the case with tantalum. However, the concentration of titanium has been limited, on the one hand, by the fact that the element can have a negative effect on the resistance to oxidation and, on the other hand, because an excessively high concentration of titanium can lead to a destabilisation of the  $\gamma'$  phase. The total of the concentrations of tantalum, titanium and aluminium roughly determines the volume fraction of the  $\gamma'$  hardening phase. The concentrations of those three elements have been adjusted in order to optimise the volume fraction of the  $\gamma'$  phase, while keeping the  $\gamma$  and  $\gamma'$  phases stable when maintained for long periods at elevated temperature, and taking into consideration the fact that the concentration of chrome has been fixed at approxi-

mately 12% by weight in order to achieve the desired resistance to corrosion.

Alloy SCB444 has been produced in the form of monocrystals having orientation  $\langle 001 \rangle$ . The density of that alloy has been measured and found to be equal to  $8.22 \text{ g.cm}^{-3}$ .

After directional solidification, the alloy is substantially constituted by two phases: the austenitic matrix  $\gamma$ , which is a solid nickel-based solution, and the  $\gamma'$  phase, which is an intermetallic compound whose basic formula is  $\text{Ni}_3\text{Al}$  and which precipitates mainly within the  $\gamma$  matrix in the form of fine particles measuring less than 1 micrometre during cooling to the solid state. A small fraction of the  $\gamma'$  phase is also located within solid particles resulting from a liquid eutectic transformation  $\rightarrow \gamma + \gamma'$  once solidification has ended. The volume fraction of the  $\gamma/\gamma'$  eutectic phase is in the order of 1.4%.

Alloy SCB444 underwent homogenising heat treatment at a temperature of  $1270^\circ\text{C}$  for 3 hours with cooling in air. This temperature is higher than the solvus temperature of the  $\gamma'$  phase (dissolution temperature of the precipitates of the  $\gamma'$  phase), which is  $1253^\circ\text{C}$ , and less than the solidus temperature, which is  $1285^\circ\text{C}$ . The treatment is intended to dissolve all of the precipitates of the  $\gamma'$  phase, whose distribution of sizes is very wide in the coarse state of directional solidification, to eliminate the solid  $\gamma/\gamma'$  eutectic particles and to reduce the chemical heterogeneities which are associated with the dendritic solidification structure.

The interval between the  $\gamma'$  solvus temperature of the alloy SCB444 and its solidus temperature is very large, which al-

allows ready application of the homogenising treatment without any risk of melting and with the certainty of obtaining a homogeneous microstructure which allows optimised resistance to creep.

The cooling which follows the homogenising treatment described above was carried out by hardening in air. In practice, the rate of this cooling must be so high that the size of the particles precipitated during the cooling operation is less than 500 nm.

The homogenising heat treatment procedure which has just been described is an example which allows the intended result to be achieved, that is to say, a homogeneous distribution of fine particles of the  $\gamma'$  phase whose size is no greater than 500 nm. This does not exclude the possibility of obtaining a similar result by using a different treatment temperature provided that the temperature lies within the range separating the  $\gamma'$  solvus temperature and the solidus temperature.

Alloy SCB444 was tested after undergoing a homogenising treatment as described above, then two annealing treatments which allow the size and the volume fraction of the precipitates of the  $\gamma'$  phase to be stabilised. A first annealing treatment consisted in heating the alloy to 1100°C for 4 hours with cooling in air, which leads to stabilisation of the size of the precipitates of the  $\gamma'$  phase. A second annealing treatment at 850°C for 24 hours, followed by cooling in air, allows the volume fraction of the  $\gamma'$  phase to be optimised. This volume fraction of the  $\gamma'$  phase is estimated at 57% in alloy SCB444. Once all of the heat treatments are

completed, the  $\gamma'$  phase has been precipitated in the form of cuboid particles whose size is between 200 and 500 nm.

Cyclical hot-corrosion tests were carried out at 900°C on alloy SCB444 on an industrial corrosion bench with a burner. The cycle was as follows: 1 hour at 900°C in the corrosive atmosphere produced by the burner, then 15 minutes out of the oven at ambient temperature. The burner operated with fuel loaded with 0.20% sulphur. A saline water solution at 0.5 g.l<sup>-1</sup> NaCl was vaporized on the test piece at a rate of 2.2 m<sup>3</sup>.h<sup>-1</sup>. The test piece was coated every 100 hours with a deposit of 0.5 mg.cm<sup>-2</sup> Na<sub>2</sub>SO<sub>4</sub>. For comparison, alloys IN738 and IN792 were tested at the same time. The criterion for corrosion resistance is the number of cycles for which the first corrosion pits appear on the surface of the test piece.

The results of the corrosion tests are illustrated by the graph in Figure 1. The start of corrosion at 900°C occurs for cycle totals which are comparable for alloys SCB444 and IN792, which fulfils the stated objective.

Tests for creep under tensile stress were carried out on machined test pieces in monocrystalline bars of orientation <001>. The bars were homogenised beforehand then annealed according to the procedures described above. Values for rupture times obtained at 750, 850 and 950°C for different levels of stress applied are listed in Table II.

Table II: Service lives with creep of alloy SCB444

Temperature (°C)	Stress (MPa)	Rupture time (h)
750	725	134
750	650	612
750	600	1152
850	500	43.1
850	425	168.5
850	300	3545/>3456
950	250	115/135
950	200	551/544
950	180	578
950	140	2109
950	120	3872

The graph in Figure 2 allows a comparison of the rupture times with creep obtained for alloys SCB444, IN738, IN792 and SC16. The stress applied is plotted on the abscissa. The value of the Larson-Miller parameter is marked on the ordinate. This parameter is given by the formula  $P = T(20 + \log t) \times 10^{-3}$ , where  $T$  is the creep temperature in Kelvin and  $t$  is the rupture time in hours. This graph shows that the creep resistance of alloy SCB444 is distinctly superior to that of alloy IN792.

The inspection of the microstructure of the test pieces of alloy SCB444 at the end of the creep tests demonstrated the absence of precipitation of fragile intermetallic particles which are rich in chrome and which are capable of appearing when maintained for sustained periods at elevated temperature in nickel-based superalloys where the  $\gamma$  matrix is over-saturated with additive elements.

Manufacturing tests on monocrystalline components of superalloy SCB444 demonstrated that it was possible to cast a large range of components whose mass can range from a few grammes to more than 10 kg, with various levels of complexity. The growth of components according to the crystallographic orientation  $\langle 001 \rangle$  is promoted and dominant and the

presence of grains that are orientated in a random manner is minimised. The liquid metal is stable in the sense that it does not react with the materials commonly used in the manufacture of moulds. The phenomenon of recrystallisation which can occur during homogenising treatment at elevated temperature is absent in the case of alloy SCB444.